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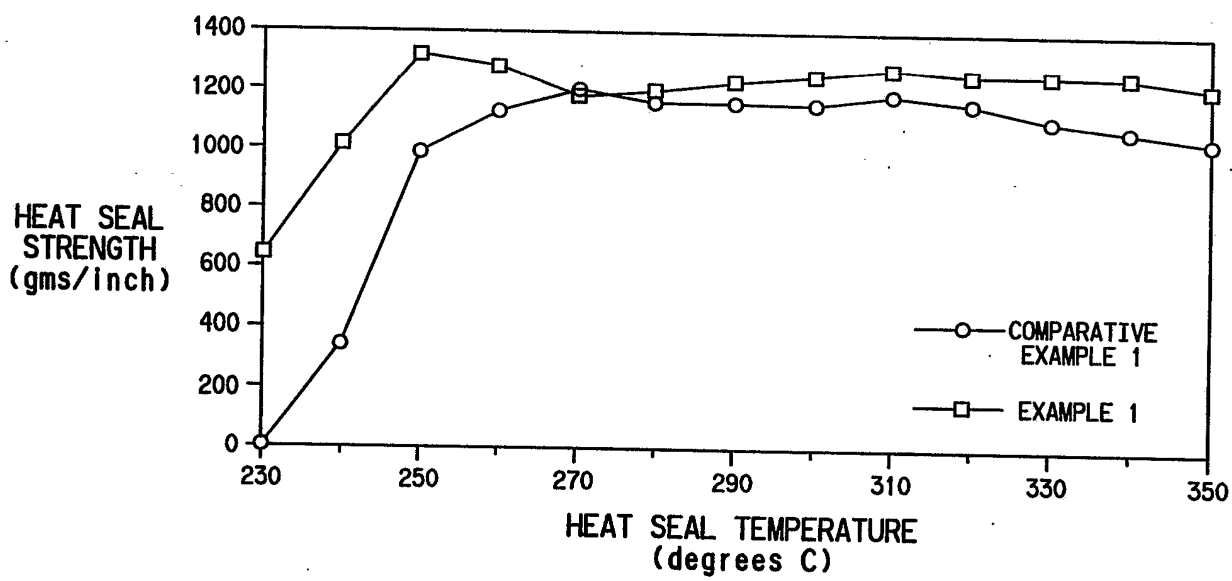
(54) Title: LAMINAR STRUCTURE OF POLYIMIDE AND LOW MELTING FLUOROPOLYMER



(57) Abstract

A laminar film structure is provided of a layer of a polyimide and at least one layer of a heat-sealable, low melting, low melt viscosity, low molecular weight tetrafluoroethylene-hexafluoropropylene copolymer, which structure is suitable in the form of narrow tapes for electrical insulation uses.

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TITLE

LAMINAR STRUCTURE OF POLYIMIDE AND LOW MELTING FLUOROPOLYMER

BACKGROUND OF THE INVENTION

The present invention relates to a laminar film structure of a polyimide and a low melting point, low melt viscosity heat-sealable fluoropolymer. The laminar film structure of the invention is especially useful as an insulating wire and cable wrapping having excellent high temperature properties.

Many aerospace wire and cable constructions are made using tin or silver plated conductors which are wrapped with a narrow tape of a polyimide-fluoropolymer laminar film. After wrapping, the layers of laminar film are subsequently heat-sealed together to form a continuous insulation layer on the conductor. However, the high temperatures required to heat-seal the laminar films together can result in damage to the conductor, lower wire quality and reduced process yields.

According to the present invention, there is provided a laminar film structure of a polyimide and a fluoropolymer which allows the heat-sealing temperatures to be lowered and permits wire quality to be improved. More particularly, a laminar film structure of a polyimide with a low molecular weight, low melting point, low melt viscosity fluoropolymer, specifically a copolymer of tetrafluoroethylene and hexafluoropropylene (hereinafter referred to as FEP or FEP copolymer), provides a laminar structure that heat-seals at a lower temperature than prior art polyimide-FEP laminar

structures having a higher melting point, melt viscosity and molecular weight. The polyimide-low melting FEP laminar structures of the invention are thermally durable and also exhibit improved bond retention properties after heat aging. In some cases, the bond retention values are improved by a factor of 3X over the prior art polyimide-FEP laminar structures.

Accordingly, the polyimide-low melting FEP laminar structures of the invention are particularly advantageous, since commercial wire processors can readily bond adjacent layers of the polyimide-low melting FEP laminar structure at lower heat-sealing temperatures than previously used, thereby increasing production speeds and yields and lowering production cost. The improved bond retention values after heat aging also improve thermal durability of wire insulated with the laminar structures.

Laminar structures of a polyimide and a fluorinated ethylene-propylene copolymer are well-known in the prior art and are disclosed, for example, in U.S. 3,592,714; U.S. 3,684,646 and U.S. 3,352,714.

U.S. 3,592,714, issued to Katz on July 13, 1971, discloses a laminar structure of a layer of a polyimide and a layer of a copolymer containing from 5 to 50 weight % hexafluoropropylene and from 50 to 95 weight % of tetrafluoroethylene for use as an electrical insulation. A layer of an organosilane is applied to the polyimide in order to improve adhesion of the polyimide layer to the FEP copolymer layer.

U.S. 3,684,646, issued to Kreuz et al. on August 15, 1972, discloses a laminar structure, suitable for use in the form of narrow tapes as an electrical insulation, comprising a base layer of a non-heat

sealable polyimide, a layer of a heat-sealable polyimide and a layer of a copolymer containing from 5 to 50 weight % of hexafluoropropylene and from 50 to 95 weight % of tetrafluoroethylene.

U.S. 3,352,714, issued to Anderson et al. on November 14, 1967, discloses a laminar structure of a polyimide and a surface activated copolymer of tetrafluoroethylene and hexafluoropropylene containing at least 5 weight % of hexafluoropropylene.

None of the aforesaid prior art patents, however, discloses the low molecular weight, low melting point, low melt viscosity FEP copolymers used in the laminar structures of the invention and which provide lower heat-sealing processing temperatures and improved bond retention properties after heat aging. Moreover, it is considered both surprising and unexpected that a lowering of the heat sealing processing temperature and an increase in the bond strength occurs using the low melting, low melt viscosity FEP copolymers used in the laminar structures of the invention as compared to the higher melting, higher melt viscosity FEP copolymers used in the prior art laminar structures.

SUMMARY OF THE INVENTION

According to the present invention, there is provided a laminar film structure for use as a high temperature insulative wrapping comprising a layer of a polyimide and at least one layer of a heat-sealable tetrafluoroethylene-hexafluoropropylene copolymer, said copolymer consisting essentially of from 84 to 87 weight % of tetrafluoroethylene and from 13 to 16 weight % of hexafluoropropylene and having a melting point ranging

from 230 to 255°C, and a melt viscosity ranging from 16,000 to 60,000 poises.

DESCRIPTION OF THE DRAWINGS

Figure I graphically compares the heat-seal bond strength as a function of heat-seal temperature of a laminar film structure of the invention to a laminar structure of the prior art.

Figure II graphically shows the % of heat-seal bond strength retention after thermal aging for a laminar film structure of the prior art.

Figure III graphically shows the % of heat-seal bond strength retention after thermal aging for a laminar film structure of the invention.

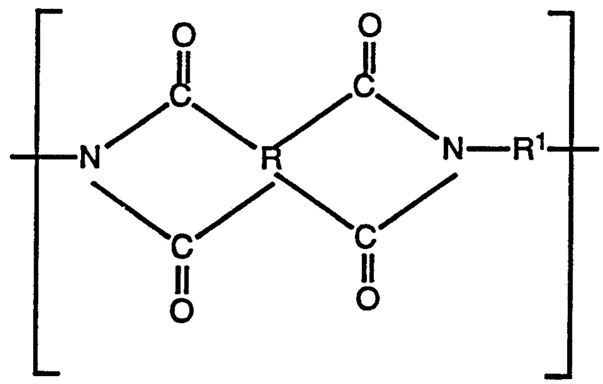
Figure IV graphically compares the heat-seal bond strength at elevated temperatures of a laminar film structure of the invention to a laminar film structure of the prior art.

DETAILED DESCRIPTION OF THE INVENTION

The laminar film structure of this invention finds special use in insulating wires or cables of electrical conductors wherein the structure is wrapped around the wire and is then heat sealed to form a continuous coating. The polyimide layer provides electrical insulation with high temperature stability and at least one fluoropolymer layer provides additional electrical insulation and serves as a heat-sealing adhesive.

The polyimide used in the laminar structure of the invention is derived from the reaction of an aromatic

tetracarboxylic dianhydride and an aromatic diamine and contains the following recurring structural unit:



wherein R is a tetravalent aromatic organic radical and R^1 is a divalent aromatic radical.

Such polyimides and their polyamide acid precursors are more fully described in U.S. 3,179,164 and U.S. 3,179,634 which are incorporated herein by reference. A particularly preferred polyimide is derived from pyromellitic dianhydride and 4,4'-diaminodiphenyl ether.

The polyimide layer must be thick enough to provide adequate electrical insulation properties and film strength and integrity but must be thin enough to be flexible and mold closely to articles wrapped by the structure. For most uses, the thickness of the polyimide layer ranges from 7.2 to 72 microns, preferably from 18 to 50 microns.

The fluoropolymer constitutes a critical component of the laminar structures of the invention and is a copolymer of tetrafluoroethylene (TFE) and hexafluoropropylene (HFP) containing from 84 to 87 weight % of tetrafluoroethylene and from 13 to 16 weight % of hexafluoropropylene. Copolymers containing varying proportions of TFE and HFP within the above ranges can

be used as long as the final copolymer has a melt viscosity ranging from 16,000 to 60,000 poises.

The particular fluoropolymer preferred for use in the laminar structures of the invention has been found to provide improved results over other fluoropolymers which are known and available. For example, it is important that the fluoropolymer layer has a melting point ranging from 230 to 255°C to avoid degradation of electrical cable components and metal wire coatings of tin, nickel or silver during the insulation winding and sealing processes. Relatively higher melting fluoropolymers are not satisfactory for use in this invention. A preferred tetrafluoroethylene-hexafluoropropylene copolymer used in this invention contains about 13.6 weight % hexafluoropropylene and has a melting point of 245°C and a melt viscosity of 28,000 poises.

The fluoropolymer layer provides heat seal adhesion for the polyimide layer when the structure is wrapped around a wire or cable or the like. As a heat sealing adhesive, it has been found that at least one layer of fluoropolymer having a thickness of from 1 to 12 microns is most effective and thicknesses of from 2 to 6 microns are preferred. Too little of the fluoropolymer adhesive causes inadequate heat seal bond strength and too much requires inordinately long sealing times at elevated temperatures in formation of the heat seal.

The fluoropolymer layer is conveniently applied to one or both sides of the polyimide as an aqueous polymer dispersion. More specifically, the fluoropolymer can be applied to the polyimide as a layer about 10 to 50 microns thick as an aqueous dispersion of a colloidal copolymer of tetrafluoroethylene and

hexafluoropropylene, said copolymer having a hexafluoropropylene content of 13 to 16 weight % and a specific melt viscosity of from 16,000 to 60,000 poises, said dispersion having a solids content of from 10 to 30 %, at a temperature in the range from room temperature up to about 60°C and heating the laminar structure at a temperature ranging from 350 to 450°C, preferably 390 to 420°C, for a period of about 0.2 to 15 minutes, preferably 0.5 to 2.0 minutes.

It has been found that the form of the laminar structure of this invention is more important than the method for making it. While the examples which follow show preparation of the laminar structure of the invention by coating dispersions of a fluoropolymer onto a polyimide film, the laminar structure can also be prepared by coextruding the fluoropolymer and polyimide layers or by laminating separate and individual fluoropolymer film and polyimide film layers together.

The laminar film structure of the invention is useful for electrical insulation purposes. The structures are preferably slit into narrow widths to provide tapes. The tape is wound around the electrical conductor in spiral fashion and overlapping on itself. The amount of overlap can vary, depending on the angle of wrap. The tension employed during the wrapping operation can also vary widely ranging from just enough tension to prevent wrinkling to a tension high enough to stretch and neck down the tape. Even when the tension is low a snug wrap results since the tape shrinks to a certain extent under the influence of heat during the ensuing heat-sealing operation. Heat-sealing of the tape is accomplished by treating the tape-wrapped conductor at a temperature and for a time sufficient to

fuse the FEP copolymer layer of the construction. The heat-sealing temperature required can range from about 240 to 400°C depending on the insulation thickness, the number of layers of insulation, the gauge of the metal conductor, the speed of the production line and the length of the sealing oven.

The utility of the laminar film structures of the invention is in general similar to that of other well-known polyimide films. For example, tapes of the laminar film structures of various widths are useful as insulation when wrapped on electrical wire and cable. The film being heat-sealable, the tape can be sealed in place after wrapping and is especially useful for wire and cable which must resist exposure to high and low temperature stress.

The particular advantage of the laminar film structures of this invention over those of the prior art resides in obtaining maximum bond strength at lower heat-sealing temperatures and retention of the bond strength after thermal aging.

The principle and practice of the present invention will now be illustrated by the following examples which are provided to illustrate the practice and use thereof.

EXAMPLE 1 (COMPARATIVE EXAMPLE 1)

A 25 microns thick polyimide film (sold by E. I. du Pont de Nemours and Company under the trademark Kapton® HN) was coated on both sides with an aqueous dispersion of a low melting, low melt viscosity FEP copolymer of the invention and directly compared to a 25 microns thick polyimide film coated on both sides with an aqueous dispersion of a higher melting, high melt

viscosity FEP copolymer of the prior art. The thickness of the FEP copolymer layers was 2.5 microns.

The FEP copolymer layers were applied to the polyimide layer by coating the following aqueous dispersions of the respective FEP copolymers on the polyimide layer and then drying the coatings and coalescing the FEP copolymer particles to yield continuous coatings:

Dispersion A (Example 1) - A 20 weight % dispersion of a FEP copolymer containing 13.6 weight % hexafluoropropylene and 86.4 weight % tetrafluoroethylene having a melting point of 245°C and a melt viscosity of 28,000 poises.

Dispersion B (Comparative Example 1) - A 20 weight % dispersion of an FEP copolymer containing 11.8 weight % of hexafluoropropylene and 88.2 weight % of tetrafluoroethylene having a melting point of 263°C and a melt viscosity of 85,000 poises.

Heat-seal strengths of samples of both laminar film structures were measured using a robot heat sealer. Two 15 x 25 cm samples of laminar film were placed in superposed relation so that opposing FEP copolymer surfaces were in contact. The superimposed films were then sealed together using a sealing bar heated at 230 to 350°C at 100 psi contact pressure for 20 seconds. The heat-sealed film samples were tested for heat-seal strength by securing the free ends thereof in an Instron tensile tester and pulling the samples apart. The highest force in grams required to pull the strips apart was taken as a measure of the heat-seal bond strength.

The heat-seal results are presented graphically in Figure I and show that the polyimide-FEP copolymer laminar structure of Example 1 achieves maximum bond strength at much lower heat-seal temperatures when compared to the polyimide-FEP copolymer laminate structure of Comparative Example 1 of the prior art.

Thermal aging tests were conducted to determine the seal retention performance of the laminar structures after aging in a hot air atmosphere for long periods of time. Samples of the laminar film structure of Example 1 were heat sealed in a robotic heat-sealer at 270°C and samples of the laminar film structure of Comparative Example 1 were similarly heat-sealed at 290°C. Samples of the heat-sealed laminar films were then placed in air atmosphere ovens and thermally aged at temperatures of 150°C, 200°C and 230°C for from 1 to 6 weeks. The bond strengths of the thermally aged, heat-sealed laminar films were determined as previously described and are shown graphically in Figure II for Comparative Example 1 of the prior art and in Figure III for Example 1 of the invention. The results show that the heat-seal bond strength retention of the thermally aged laminar film of Example 1 was significantly better than the laminar film of Comparative Example 1. The results were clearly surprising, since laminar structures containing FEP copolymers having a lower melting point, lower molecular weight and lower melt viscosity would be expected to have lower thermal durability than laminar structures containing FEP copolymers having a higher molecular weight, higher melt viscosity and higher melting point.

Finally, the bond strengths of the laminar film structures of Example 1 and Comparative Example 1 were determined at elevated temperatures corresponding to

high temperature wire insulation processing environments. The laminar film structures of Example 1 and Comparative Example 1 were heat-sealed at 270°C and 290°C, respectively, as previously described. The heat-sealed films were then exposed to temperatures of from 25° to 200°C. Since the FEP copolymer used in the laminar structure of Example 1 had a lower melting point, melt viscosity and molecular weight than the FEP copolymer used in Comparative Example 1, the Comparative Example was expected to have significantly better heat seal strength in this test. The heat-seal strength results are depicted graphically in Figure IV and, surprisingly, show that there was no significant difference in bond strengths at elevated temperatures between the laminar structures of Example 1 and Comparative Example 1.

WHAT IS CLAIMED IS:

1. A laminar film structure for use as a high temperature insulative wrapping comprising a layer of a polyimide and at least one layer of a heat-sealable tetrafluoroethylene-hexafluoropropylene copolymer, said copolymer consisting essentially of from 84 to 87 weight % of tetrafluoroethylene and from 13 to 16 weight % of hexafluoropropylene and having a melting point ranging from 230°C to 255°C, and a melt viscosity ranging from 16,000 to 60,000 poises.

2. The laminar film structure of Claim 1 wherein the copolymer comprises about 13.6 weight % hexafluoropropylene and about 86.4 weight % of tetrafluoroethylene and has a melting point of about 245°C and a melt viscosity of about 28,000 poises.

3. The laminar film structure of Claim 1 wherein the polyimide is derived from pyromellitic dianhydride and 4,4'-diaminodiphenyl ether.

4. The laminar film structure of Claim 1 wherein layers of tetrafluoroethylene-hexafluoropropylene copolymer are affixed to both sides of the polyimide layer.

5. The laminar film structure of Claim 4 wherein the polyimide layer has a thickness of from 7.2 to 70 microns.

6. The laminar film structure of Claim 4 wherein the tetrafluoroethylene-hexafluoropropylene copolymer layers have a thickness of from 1 to 12 microns.

7. A wire or cable spirally wrapped by a strip of a laminar film structure comprising a layer of a polyimide and at least one layer of a heat-sealable tetrafluoroethylene-hexafluoropropylene copolymer, said copolymer consisting essentially of from 84 to 87 weight

% of tetrafluoroethylene and from 13 to 16 weight % of hexafluoropropylene and having a melting point ranging from 230° to 255°C, and a melt viscosity ranging from 16,000 to 60,000 poises, wherein the edges of the strip of the laminar film structure overlap and the strip has been heat-sealed to itself at the overlapped edges.

8. The wire or cable of Claim 7 wherein layers of tetrafluoroethylene-hexafluoropropylene copolymer are affixed to both sides of the polyimide layer.

9. The wire or cable of Claim 8 wherein the copolymer comprises about 13.6 weight % hexafluoropropylene and about 86.4 weight % of tetrafluoroethylene and has a melting point of about 245°C and a melt viscosity of about 28,000 poises.

FIG.1

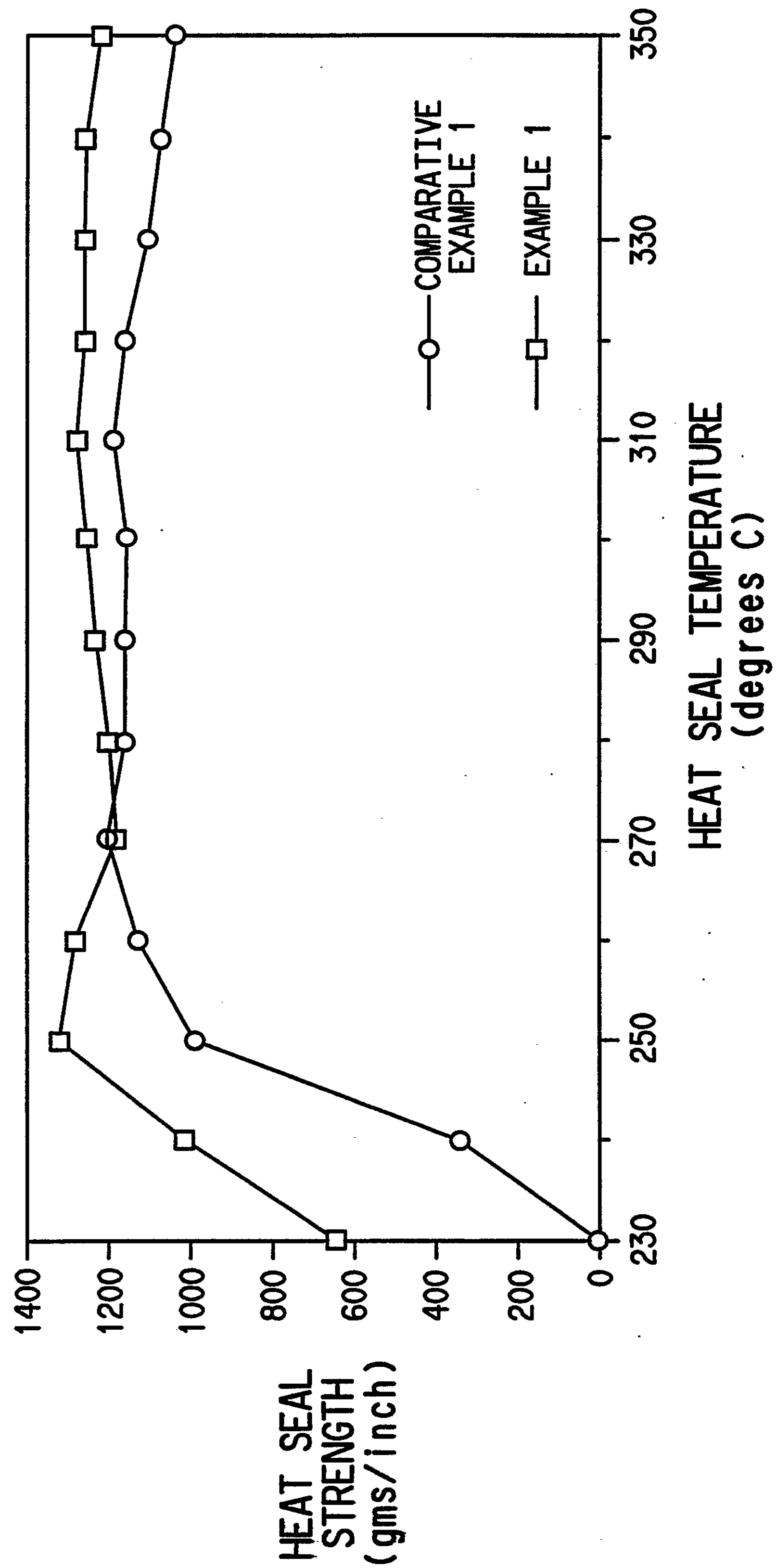

HEAT SEAL STRENGTH (gms/inch)
1400
1200
1000
800
600
400
200
0
230
250
270
290
310
330
350
HEAT SEAL TEMPERATURE (degrees C)
COMPARATIVE EXAMPLE 1
EXAMPLE 1

FIG.2

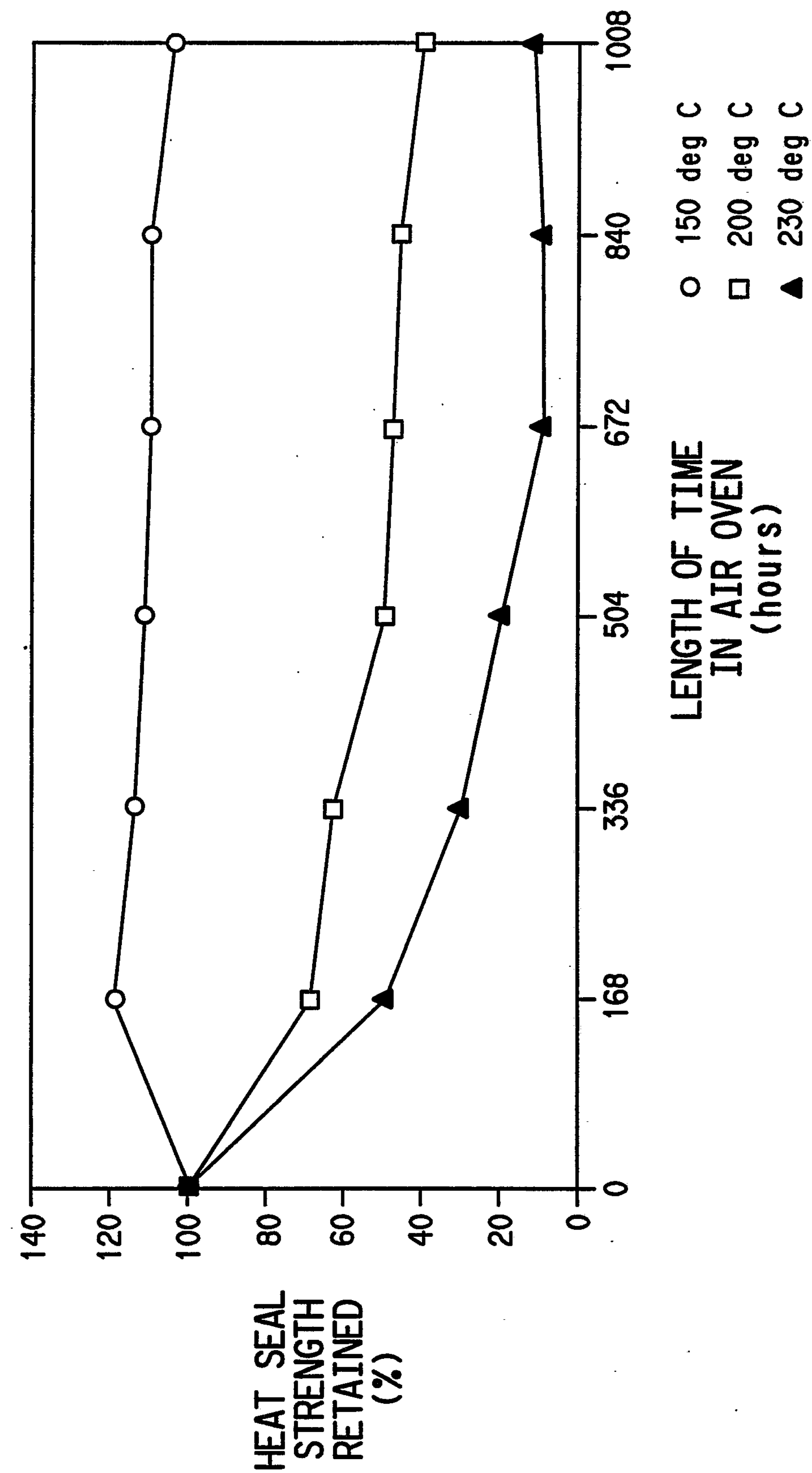

HEAT SEAL
STRENGTH
RETAINED
(%)
140
120
100
80
60
40
20
0
0
168
336
504
672
840
1008
LENGTH OF TIME
IN AIR OVEN
(hours)
150 deg C
200 deg C
230 deg C

FIG.3

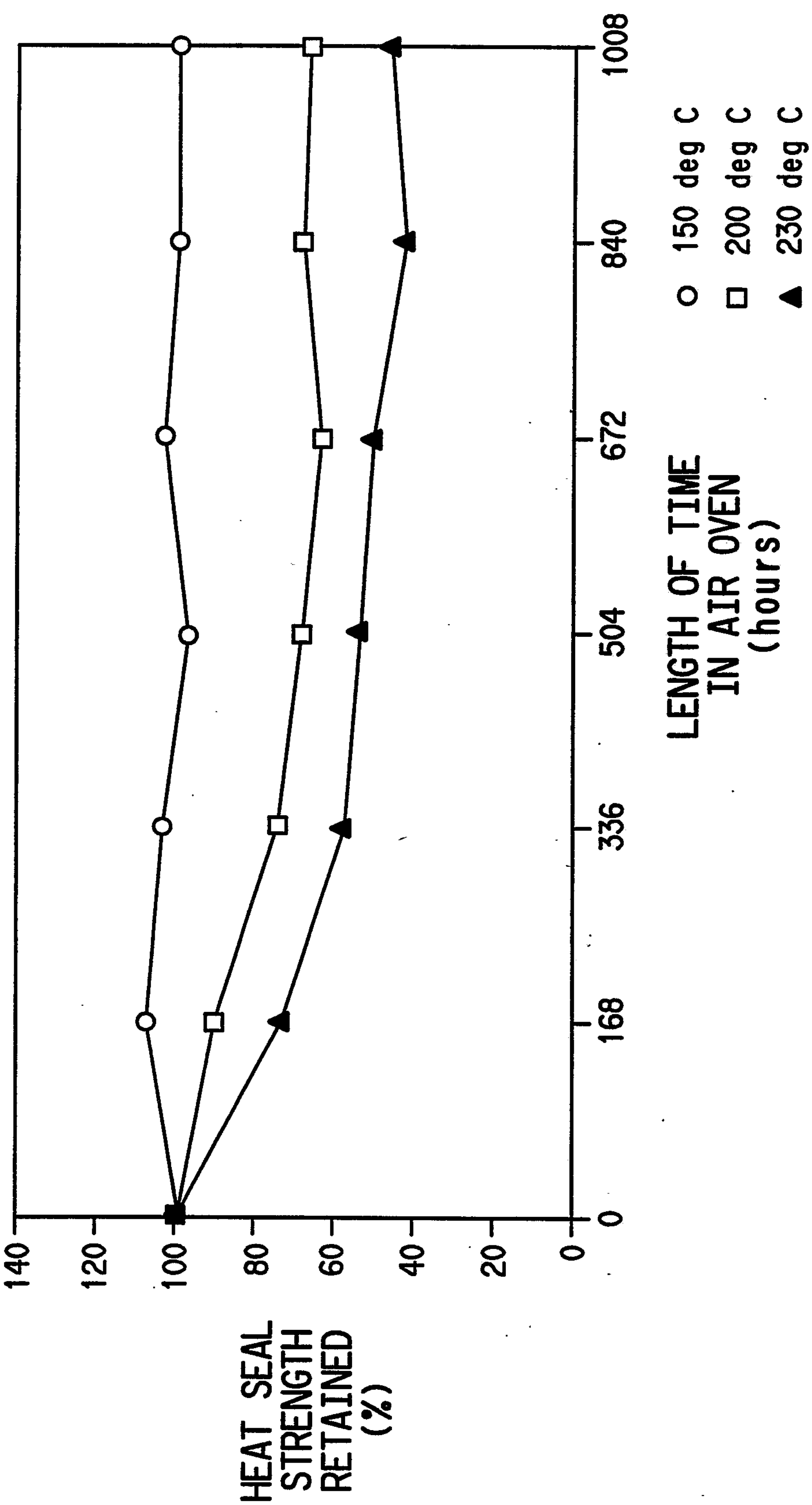
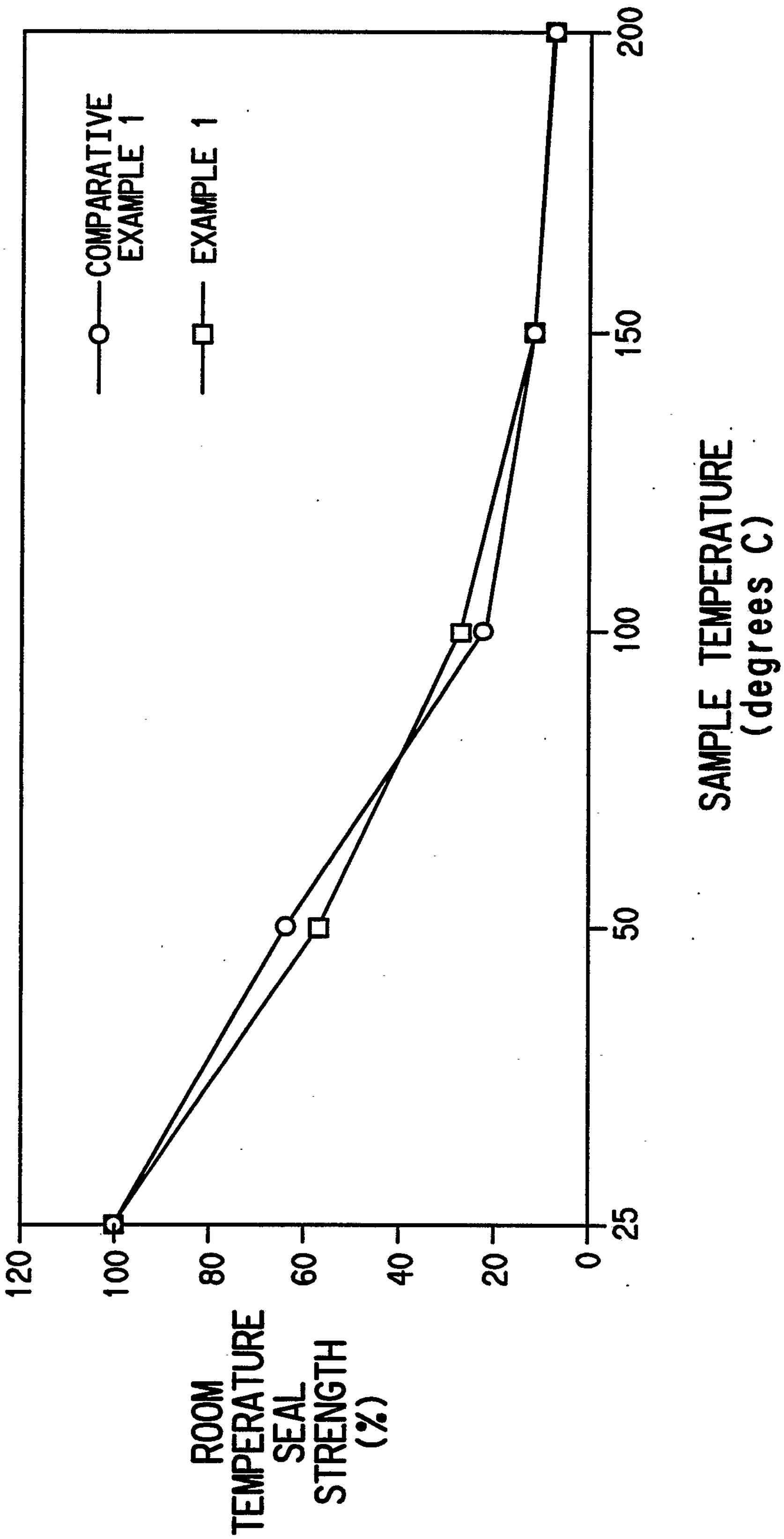

HEAT SEAL STRENGTH RETAINED (%)
140
120
100
80
60
40
20
0
0
168
336
504
672
840
1008
LENGTH OF TIME IN AIR OVEN (hours)
150 deg C
200 deg C
230 deg C

FIG.4


COMPARATIVE EXAMPLE 1
EXAMPLE 1
ROOM TEMPERATURE SEAL STRENGTH (%)
0
20
40
60
80
100
120
SAMPLE TEMPERATURE (degrees C)
25
50
100
150
200

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 92/11295

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC^5: B 32 B 27/32,B 32 B 27/28,H 01 B 3/30

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC^5	B 32 B,H 01 B,C 08 J

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category [*]	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	GB, A, 1 126 012 (DU PONT DE NEMOURS AND COMPANY) 05 September 1968 (05.09.68), claims. --	1-9
X	EP, A1, 0 467 096 (E.I. DU PONT DE NEMOURS AND COMPANY) 22 January 1992 (22.01.92), claims; page 4, lines 35-36; page 5, lines 4-28. --	1-9
X	EP, A2, 0 072 223 (E.I. DU PONT DE NEMOURS AND COMPANY) 16 February 1983 (16.02.83), claims; page 2, line 30; examples 5,6. ----	1-4, 7-9

* Special categories of cited documents: [10]

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IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
14 April 1993	29 APR 1993
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	WEIGERSTORFER e.h.

ANHANG

zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

ANNEX

to the International Search Report to the International Patent Application No.

ANNEXE

au rapport de recherche international relatif à la demande de brevet international n°

PCT/US 92/11295 SAE 69145

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Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
GB A 1126012		keine - none - rien	
EP A1 467096	22-01-92	JP A2 4232741	21-08-92
EP A2 72223	16-02-83	CA A1 1201945	18-03-86
		DE C0 3277874	04-02-88
		EP A3 72223	10-10-84
		EP B1 72223	23-12-87
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		JP B4 1011463	23-02-89
		SU A3 1436894	07-11-88
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